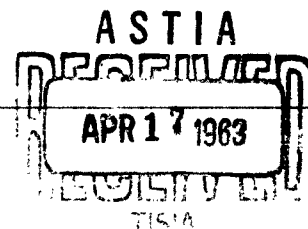AID Report T-63-46 ;

3 April 1963

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MAGNETO-OPTICS OF RARE-EARTH IONS
IN FERROMAGNETIC CRYSTALS

(Proposed Controllable Ferromagnetic Lasers)

Translation

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MAGNETO-OPTICS OF RARE-EARTH IONS IN FERROMAGNETIC CRYSTALS

*The following article presents an experimental and
theoretical investigation of ferrite garnet crystals
doped with rare-earth ions and subject to an external
magnetic field. According to the author, the energy
level structure of such a system, based on the ex-
change interaction effect, lends itself to the design
of an inherently controllable infrared laser.*

1. ## Faraday Effect Based on Exchange Splitting of Energy Levels in Ferromagnetics.

The preceding work (Ref. 1) on measuring the absorption of cir-
cularly polarized light in a magnetized europium garnet showed that
exchange interactions between the ions of the iron and rare-earth
sublattices produce circular dichroism resonating within the euro-
pium absorption line $^7F_0 \rightarrow {}^7F_6$. However, the quantitative evalua-
tion of these magneto-optical effects in the ferromagnetic crystals,
especially of the Faraday effect, calls for the determination of the
double circular refraction $\Delta n_\pm = n_+ - n_-$. It is very difficult to
measure directly this value for low-intensity absorption lines, since
it is very small (Δn_{max} being of the order of 10^{-3}). Therefore, using
the classical dispersion theory, we shall attempt to determine from
experimental curves of circularly polarized light absorption the
value of the double circular refraction in europium garnet caused by
exchange interaction.

With the use of some simplifying assumptions, the classical
theory yields the following formulas for the refraction and absorp-
tion indices within the region of the absorption line (Ref. 2):

$$n - 1 = -a \frac{x}{1 + x^2} , \tag{1}$$

$$k = a \frac{1}{1 + x^2} , \tag{2}$$

where $x = 2(\omega - \omega_0)/\gamma$, ω_0 being absorption line frequency and γ the
attenuation constant characterizing the width of the absorption line;

and a is the coefficient determining the intensity of the absorption
line. The above formulas show that the dispersion curve in the re-
gion of the absorption line can be obtained from a known experimental
absorption curve. Consequently, having obtained the values of n_+ and
n_- from the experimental absorption curves for right-handed and left-
handed circularly polarized light, one can find Δn_+ and compute the
curve of the Faraday effect in the region of the europium absorption
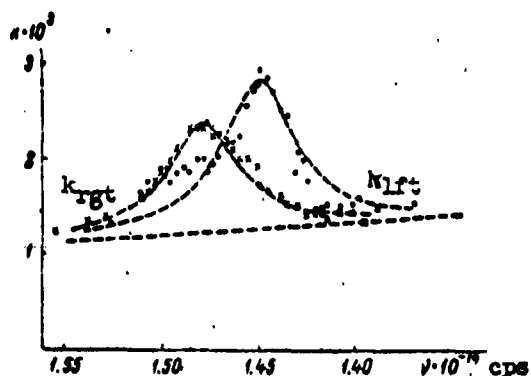line.

Fig. 1. Absorption coefficient of
circularly polarized light in euro-
pium garnet magnetized in the longi-
tudinal direction

Fig. 1 shows the curves of absorption coefficients for circularly
polarized light obtained from experimental curves corrected for re-
flection from the garnet faces. (The refraction index of garnet is
assumed to be 2.2.) A dashed line shows garnet absorption curves com-
puted from equation 2 above, given the following parameters:

$$\nu_0^{rgt} = \nu_0^* = 1.478 \cdot 10^{14} \text{ cps};$$

$$a_+ = 1.14 \cdot 10^{-3};$$

$$\gamma_+/2 = 2\pi 0.027 \cdot 10^{14} \text{ cps}; \quad \text{(Cont.)}$$

$$\nu_0^{\text{lft}} = \nu_0^- = 1.447 \cdot 10^{14} \text{ cps};$$

$$a_- = 1.56 \cdot 10^{-3}; \quad \text{and}$$

$$\gamma_-/2 = 2\pi 0.027 \cdot 10^{14} \text{ cps}.$$

In the construction of theoretical curves the ground reference axis is a straight dashed line which characterizes the absorption of light by the garnet owing to reasons other than the absorption line in the europium ions under consideration. A discrepancy between the experimental and theoretical curves, connected with the asymmetry of the experimental curves, may be explained by an incomplete polarization of the circular components of light.
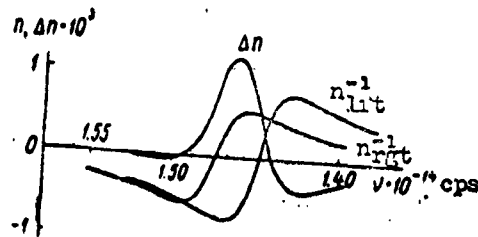

Fig. 2. Computed values of refraction index of circularly polarized light in europium garnet within the $^7F_6 \rightarrow {}^7F_0$ transition region

Fig. 2 shows the $n_+ - 1$ and $n_- - 1$ curves computed from equation 1 above, given the same parameters. The graphically determined values of Δn_+, which can be used to compute the value of Faraday rotation, since (Ref. 2)

$$\alpha_F = \frac{\pi}{\lambda} (n_+ - n_-), \tag{3}$$

are superimposed.

The values of the Faraday effect computed from equation 3 are denoted in Fig. 3 by crosses (the positive rotation if Fig. 3 has the same sign as the Faraday effect in visible light in ion, nickel, and cobalt). The solid line represents experimental values obtained previously (Ref. 1).
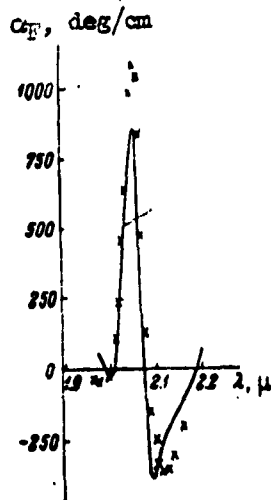
Fig. 3. Faraday effect
caused by exchange split-
ting of the $^7F_6 \rightarrow \ ^7F_0$
line in europium garnet

Therefore, the good quantitative agreement between the computed
and experimental values of the Faraday effect in the range of the Eu
garnet absorption line proves that the rotation of the infrared light
polarization plane in this region is completely due to the exchange
interaction. (The frequency of the resonance line is, of course,
determined by the spin-orbital interaction.)

Let us consider the triplet nature and the magnitude of the ex-
change splitting in somewhat greater detail.

If the effect of the internal crystalline field is neglected,
the following pattern of exchange splitting of the $^7F_0 \rightarrow \ ^7F_6$ line
should be observed. Since the total angular momentum of the ground
level equals zero, the selection rules for magnetic quantum number M
limit the transition possibilities to the three upper levels, which
have M = 0, +1, and -1 with a corresponding polarization of the
light components. Therefore, one should actually observe a Zeeman
triplet; however, the magnitude of the exchange splitting predicted
from this simple model is about three times smaller than that ob-
served experimentally. Indeed, the splitting of the line observed
in the longitudinal direction should equal

$$\Delta E \ = \ g\mu_5 H_{exch} M. \qquad (4)$$

- 4 -

When H_{exch} equals $2.5 \cdot 10^5$ oe (Ref. 1), the splitting of the two cir-cular components will yield the magnitude

$$2 \Delta E \approx 35 \text{ cm}^{-1},$$

while the experiment yields a value of 110 cm^{-1}.

The above discrepancy is apparently due to the effect of the crystalline internal field.

Let us assume, for the sake of simplicity, that the europium ion is situated in a crystalline field of cubic symmetry. Then for the point group of cubic symmetry O, the upper level of the europium ion $^7F_6$ will split in the crystalline field into one nondegenerate level A_0, one nondegenerate level A_2, one doubly degenerate level E_0, one triply degenerate level F_0, and two triply degenerate levels F_2. As expected this results in thirteen levels. The lower $^7F_0$ level is not split by the crystalline field, but its designation is changed to A_0. The selection rules for the crystal quantum number show that only transitions from A_0 to the triplet F_0 level are permitted. Therefore, the Zeeman triplet should be observed even if the crystalline field effect is taken into account, which is in agreement with the experiment. The value of the exchange splitting of the upper level F_0 will now be determined by the equation
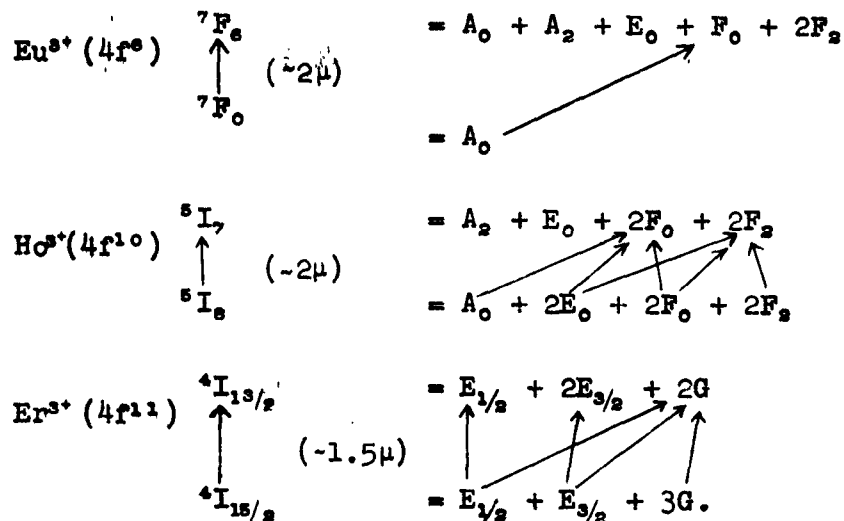
$$\Delta E = g \mu_B H_{exch} M_{eff}, \qquad (5)$$

where M_{eff} is the effective value of the magnetic quantum number. The difference between M_{eff} and M is due to the intermixing of wave func-tions with various values of M. The maximum possible value of M_{eff} is J, which in our case is 6. It should be noted that for crystals of cubic symmetry the mixing of wave functions with various values of M is particularly strong, and, therefore, we should expect a large de-parture of the value of M_{eff} from unity. To bring the equation into agreement with experiment, M_{eff} should be made equal to 3; consequently, the effect of the crystalline field allows us in principle to explain all observed features of exchange Zeeman splitting in europium garnet. The result obtained may also be considered as an experimental proof of the fact that the effective magnetic quantum number for the F_0 level in europium ion is equal to 3.

2. Controllable Optics of Rare-Earth Ions in Ferromagnetic Crystals

The agreement with experiment outlined in the preceding paragraph for the fine structure of the $^7F_0 \rightarrow {}^7F_6$ transition in europium ions, under the assumption of cubic symmetry of the crystalline field, shows that a similar approach can be applied to the analysis of the fine structure of absorption lines in other ferrite garnets.

First of all, we can now say why the fine structure of absorption lines has not been previously discovered in the study of infrared electron transitions in holmium and erbium ions (Ref. 5), in spite of the fact that the order of magnitude of exchange splitting for both of these ions is the same as in europium ions.

The following is the schematic structure of energy levels split in the cubic symmetry field, whose transitions have been investigated by the author:

$$Eu^{3+}(4f^6) \quad {}^7F_6 \uparrow \quad (\sim 2\mu) \quad {}^7F_0 \qquad = A_0 + A_2 + E_0 + F_0 + 2F_2$$
$$= A_0$$

$$Ho^{3+}(4f^{10}) \quad {}^5I_7 \uparrow \quad (\sim 2\mu) \quad {}^5I_8 \qquad = A_2 + E_0 + 2F_0 + 2F_2$$
$$= A_0 + 2E_0 + 2F_0 + 2F_2$$

$$Er^{3+}(4f^{11}) \quad {}^4I_{13/2} \uparrow \quad (\sim 1.5\mu) \quad {}^4I_{15/2} \qquad = E_{1/2} + 2E_{3/2} + 2G$$
$$= E_{1/2} + E_{3/2} + 3G.$$

The right-hand side of the diagram represents the result of splitting the lower and upper levels of the rare-earth ion in the cubic symmetry field; arrows denote dipole transitions. (It should be noted that forbidden transitions caused by both levels belonging to the same electron configuration are eliminated by the usual considerations and lead to a corresponding reduction in the probability of all transitions.)
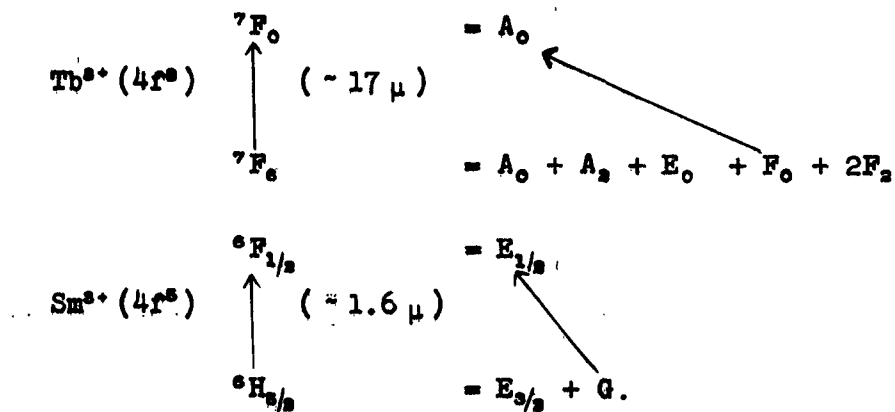
The diagram shows that while for the europium ions we should expect the Zeeman triplet corresponding to the transition between the singlet level A_0 and the triplet level F_0, for holmium and erbium ions there should be several tens of Zeeman exchange components in the same range of the spectrum, which, naturally, are not permitted, at least at room temperature. However, it does not follow that the Eu transition discussed above is unique.

It is clear that in order to observe the Zeeman exchange line structure, it is necessary to select an electron transition having

a sufficiently simple structure and to avoid overlapping between the
individual components of this line. Therefore, either the lower or
the upper energy level of the given ion should have a total angular
momentum equal or close to zero. Among the identified upper levels
of such a type in trivalent rare-earth ions are the $^3P_0$ and $^1S_0$ levels
in praseodymium and thulium, $^6F_{1/2}$ in samarium, $^5D_0$ in europium, and
$^7F_0$ in terbium. The difficulties in observing absorption lines of
rare-earth ions in the visible region of the spectrum against the
background of sharply rising iron absorption further limit the selec-
tion to the infrared transitions $^7F_6 \rightarrow {}^7F_0$ in terbium and $^6H_{5/2} \rightarrow {}^6F_{1/2}$
in samarium.

Following is an analysis of the expected fine structure of these
transitions, the polarization of individual components, and the spe-
cial features occurring in the structure of the absorption band as a
result of magnetization of the terbium and samarium garnet (the ex-
change Zeeman effect).

The splitting of Tb and Sm energy levels of interest in the
crystalline field of cubic symmetry will have the following form:

$$
\begin{array}{lcll}
& ^7F_0 & & = A_0 \\
\text{Tb}^{3+}(4f^8) & \uparrow \quad (\sim 17\,\mu) & & \\
& ^7F_6 & & = A_0 + A_2 + E_0 + F_0 + 2F_2 \\[2em]
& ^6F_{1/2} & & = E_{1/2} \\
\text{Sm}^{3+}(4f^5) & \uparrow \quad (\sim 1.6\,\mu) & & \\
& ^6H_{5/2} & & = E_{5/2} + G.
\end{array}
$$

The diagram shows that in the terbium garnet the $^7F_6 \rightarrow {}^7F_0$ line
exhibits an exchange Zeeman triplet analogous to that observed in eu-
ropium ions. The difference consists in the fact that owing to the
reverse Tb term, the lower level in this case is the triplet F_0.
This circumstance gives rise to the interesting possibility of con-
trolling the appearance of specific polarized lines in the garnet
ferrite absorption spectrum by means of an external magnetic field
at sufficiently low temperatures.

For the sake of simplicity, let us consider the case where the
lower triplet level has a total momentum equal to unity, while the
upper singlet level has a total momentum equal to zero. Moreover,

let the total momentum of the lower level be the sum of the orbital and spin momenta, where the coupling between orbital and spin momenta in the first approximation is not disrupted by the exchange field and crystalline interaction. Then the splitting of the lower level will be determined by the value of the exchange field, and the re-sulting levels will be characterized by the values of the magnetic quantum number $M = +1$, 0, and -1. Magnetization of the crystal up to saturation in the longitudinal direction at sufficiently low temperatures will orient all spins along the Z-axis and, consequently, all ions will reach an energy level having the same value of M. Let $M = +1$. The selection rules for the magnetic quantum number will then require that the transitions to the upper energy level be due only to the action of left-handed circularly polarized light. Right-handed circularly polarized light should not be absorbed by the crystal at all. The light quanta of right-handed light have a positive angular momentum and cannot transmit it to the rare-earth ions, which have a larger momentum in the lower state $(M = +1)$ than in the upper $(M = 0)$.

When the direction of magnetization of the ferromagnetic crystal is reversed, all rare-earth ions undergo a transition to the energy level with $M = -1$, and the crystal ceases to absorb left-handed light. The right-handed circularly polarized light will give rise to an absorption line shifted by $2g\mu_B H_{exch}$, where H_{exch} is the effective value of the exchange field acting on the rare-earth ions.

The same pattern should be valid in principle for the electron transition $F_0 \rightarrow A_0$ in terbium ions, since the selection rules for a crystal quantum number μ are the same as for M. The difference will consist in the substitution of the term M_{eff} for M in the formula determining splitting of the triplet level F_0. Furthermore, complications may arise when the F_0 level is not the lowest level in the terbium garnet among other Stark levels. Then, when the crystal is cooled in order to increase the population of one of the Zeeman sub-levels of the F_0 level, there will be a sharp increase in the population of the lowest Stark level and the intensity of the $F_0 \rightarrow A_0$ transition will decrease sharply.

It is quite possible that the previously noted (Ref. 1) asymmetry of the circular Zeeman exchange absorption components observed in the longitudinal direction is also due to the above cause, i.e., to the difference in the number of magnetic moments of ions directed with and against the field at room temperature. In the case of europium, all three Zeeman sub-levels of the F_0 level are practically vacant, even at room temperature and, consequently, it would seem that electron transition from the lower level, A_0, $(\mu = 0)$, stimulated by the circularly polarized light, should proceed with equal probability either to the Zeeman sub-level with $\mu = +1$ (F_{+1}), or to the sub-level with $\mu = -1$ (F_{-1}).

However, the tendency to conserve spin in electron dipole transitions — the selection rule for a spin quantum number is $\Delta S = 0$ — apparently results in a situation where electron transitions, in ions whose magnetic moment is directed along the field, are stimulated by one circularly polarized component of light, and in ions directed against the field, by the other component. In such a case, given a fixed direction of the external magnetic field and decreased temperature, an increase in the number of ions whose magnetic moments are directed along the field should lead to complete extinction of absorption of one of the polarization components. When the crystal magnetization is reversed, the observed absorption pattern for both circularly polarized light components should also reverse.

Let us now consider the special features of the $^6H_{5/2} \rightarrow {}^6F_{1/2}$ transition in trivalent samarium ions. In this case the lower energy level will be split by the cubic field into two levels, the quadruplet G and the doublet $E_{3/2}$. The electron transitions to the doublet level $E_{1/2}$, which has not been split by the cubic field, are permitted only from the quadruplet level G. The four components of the level split by the exchange field are characterized by various values of the crystal quantum number $\mu = \pm 3/2$ and $\pm 1/2$. If all the samarium ions are brought into the $\mu = + 3/2$ state (by magnetizing the crystal to saturation a depressed temperature), the absorption of right-handed polarized light in the samarium garnet will not occur at the $^6H_{5/2} \rightarrow {}^6F_{1/2}$ frequency. In the case of left-handed polarized light a single absorption line, $G_{+3/2} \rightarrow E_{+1/2}$, will be observed. In a similar manner, one may consider the number of absorption lines and their polarization when the crystal is magnetized at an angle to the Z-axis (the ions being brought into states with $\mu = + 1/2$ or $- 1/2$), and also when the exchange Zeeman effect is observed in a transverse direction.

A single difference in the nature of absorption of circularly polarized light by magnetized ferrite garnet crystals with europium, terbium, and samarium may be of interest and may be readily verified by experiment. When europium and terbium garnets will not, for example, absorb the right-handed polarized component of light for a given direction of the magnetizing field, the samarium garnet, under the same conditions, will not absorb the left-handed polarized component. This is because in Eu and Tb ions the spin direction coincides with the direction of the total angular momentum, while in samarium ions these momenta are opposed. At high temperatures this effect should produce a difference in the asymmetry of the circularly polarized light absorption line along the wavelength axis.

The magnitude of the exchange splitting of Zeeman components can be evaluated for the terbium and samarium ion levels of interest. In the case of terbium all conditions are analagous to those of europium, except for the fact that, according to Pauthenet (Ref. 6) the exchange field is approximately twice as small. Consequently, one should expect

- 9 -

that the magnitude of the splitting will also be twice as small. For the case of samarium the value of the splitting will be lower still, because of the smallness of the g-factor, which is 0.286 for the ground level.

Thus, interesting features of polarized light absorption by rare-earth ions in ferromagnetic crystals have been discussed, with concrete examples being used. We have shown how a weak external magnetic field can be used to control the appearance or disappearance of polarized absorption lines in the spectrum of a solid. Because the orbital magnetic moment of the f-shell of a rare-earth ion is coupled to spin, a constant external magnetic field changes the orientation of the spontaneous magnetization vector and, consequently, changes the population of certain energy levels important in electron dipole transitions. It is possible therefore, that the exchange Zeeman effect may be utilized in optical masers (lasers) or in quantum light indicators (Ref. 7) in a manner similar to that in which the Zeeman effect in the external magnetic field has been applied to microwave masers. For example, having used the above method to fill completely the F_{+1} level of trivalent terbium ions and, therefore, having created a zero population in the F_{-1} level, one can then pump the system with right-handed polarized infrared light to effect electron transitions from the F_{+1} level to the A_0 level, to create negative temperature at the A_0 and E_{-1} levels, and to obtain conditions favorable for the generation of left-handed polarized light corresponding to the stimulated transitions $A_0 \rightarrow F_{-1}$. It is clear that such a laser based on the ferromagnetic crystal can be controlled by an external magnetic field. By switching off or decreasing the external magnetic field, one can transfer a major portion of the electrons from the F_{+1} to the F_{-1} level and, therefore, disrupt the stimulated emission $A_0 \rightarrow F_{-1}$. Such a method will make it possible to vary the intensity of stimulated emission of the laser by 100%, using the external magnetic field.

In such a laser one can also tune the frequency or effect frequency modulation of the stimulated emission by compressing the crystal and thereby changing the magnitude of the exchange integral and, comsequently, the frequency of the $A_0 \rightarrow F_{-1}$ transition.

It is quite clear that if we could succeed in exciting the luminescence spectrum of rare-earth ions in a ferromagnetic crystal, all the above effects could be observed in the spectrum of polarized luminescence. Such a work could then be directly related to the research on polarized luminescence (Ref. 8) carried out to determine the nature of absorption and orientation of absorption centers in crystals. The special feature of ferromagnetic crystals consists in the fact that there is a possibility of changing the orientation of absorbing centers in the crystal by means of the external magnetic field and thus controlling the spectrum of polarized luminescence of the crystal.

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Submitted to the Editor 4/16/62.

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